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Eutrophication in Coastal New Zealand Lakes and the Mitigation Potential of Phosphorus Immobilisation Using Clay Based Amendments.

A Dissertation

submitted in partial fulfilment

of the requirements for the Degree of

Bachelor of Agricultural Science with Honours

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Samuel Whitley

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Abstract of a Dissertation submitted in partial fulfilment of the requirements for the Degree of Bachelor of Agricultural Science with Honours.

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by

Samuel Whitley

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Water amendments were analysed in-vitro to identify their potential for phosphate sequestration in coastal lakes and water bodies, in an effort to reduce their phosphorus levels.

The potential amendments were identified: Allophane, Bauxsol™ (re-purposed from aluminium processing) and Phoslock™ (lanthanum treated Bentonite), along with several other clays such as Kaolinite, Bentonite, and Illite as a comparison.

Each Amendment was placed in a solution of phosphate, agitated, then left to settle over 24 hours. The remaining phosphate in the solution was measured with a UV spectrometer (880nm, ascorbic acid analysis). The results showed that the common clays (kaolinite, Bentonite, illite) had very low adsorbance potential, with an average of 6.15ppm of phosphate adsorbed out of a total of 50ppm, Phoslock™ adsorbed 33.7ppm while allophane and Bauxsol™ adsorbed 11ppm out of 50 ppm. The adsorption experiment was then repeated at variable pHs'.

The experiment showed that Phoslock™ was the most effective at adsorbing phosphorus, and has an adsorption coefficient two orders of magnitude above the common clays, and has great potential for use in the lake. Allophane and Bauxsol™ also show promise, however at higher pHs' their adsorption capability was hindered. Further experiments will need to focus on a final evaluation of Phoslock™'s effectiveness in reducing Phosphorus levels in the lake.

Keywords: Phosphate, Water quality, Environment, Cultural values, Adsorption Isotherm, pH, Te Waihora, Te Roto o Wairewa, Forsyth, Ellesmere.

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Chapter 1

Introduction

Water quality is defined by the respective values that society attributes to water bodies. Because of the great variability of water bodies 'quality' is not an easy concept to define. To determine the state of a water body, values need to be identified that inform decision making. These values can be defined as human ascribed values or ecological values. Human values include recreational, cultural, and aesthetic. In particular, Lake Ellesmere (Te Waihora) has cultural and spiritual significance to the South Island Maori Iwi, particularly Ngai Tahu, and is a traditional source of *Mahinga Kai (Kitto, 2010).* Ecological values include measures such as biodiversity and ecosystem services provided by lake systems. Anzecc (2000) states that the principles behind creating guidelines for water quality are to 'conserve a community's resources' maintain 'ecological processes, on which life depends' while increasing total quality of life, or put another way: the commission 'aims to meet the needs of today, while conserving our ecosystems to the benefit of future generations.'

From 1989 to 2000, nitrogen and phosphorus in waterways increased sharply. However, they stabilised between the period of 2000 and 2009. In contrast, visual clarity increased over the 21 year period, attributed mainly to soil conservation methods and riparian fencing (Ballantine & Davies-Colley, 2014). Over the spatial dimension, there is a strong correlation between the percentage of a catchment in pasture and its water quality, despite variability in soils topography and climate. Under pasture water clarity improves, but the nutrient concentrations increase. As pastoral production systems are intensified, and more land is put into pasture, there is a build-up of nutrients in rivers, which ends up in the sea or lakes. Cropping is also correlated with higher levels of nutrients in river water and causes reduced water clarity due to erosion being exacerbated (Davies-Colley, 2013).

Action has been taken to improve the value surrounding waterways, particularly to do with managing nutrient levels and erosion. Fencing off waterways on farms, preventing effluent overloading and planting riparian strips reduce the amount of direct transfer of animal waste and organic phosphorus and nitrate into waterways. Improved understanding of these processes has also contributed to maintaining good soil structure and planting catch crops further reducing nutrient losses from farms and the erosion of waterways. (Jenkins, 2016; Reid et al., 2004; Schallenberg et al., 2010; Smith & Schindler, 2009)

This research is focusing on lakes Ellesmere (Te Waihora) and Forsyth (Te Roto o Wairewa), both of which face serious problems caused by water quality degradation and eutrophication. The research is looking at methods to remove phosphorus from the water column with the use of adsorbing

amendments such as Phoslock™, Bauxsol™, and allophane, and identify potential solutions to the problems facing these coastal New Zealand Lakes.

Chapter 2

Literature Review

2.1 Eutrophication

Due to a lakes' positions in the landscape, they tend to be poorly flushed ecosystems (Monbet et al., 2007). As a result, once nutrients enter lakes from the catchment they become concentrated. This phosphorus is essential to the lake ecosystems and provides the basis for aquatic plants and phytoplankton, on which the aquatic ecosystem depends (Bennett & Schipanski, 2013). Due to the reactive nature of phosphorus, it is quickly adsorbed and occluded. The phosphorus reacts with iron and aluminium oxides on the surface of clays, organic matter or is taken up by biota (Swanson, 2014). These mechanisms cause phosphorus to reach an equilibrium where phosphorus entering the system equals the amount of phosphorus being buried and made unavailable by incoming sediment. Nitrogen species entering the lake can be converted into atmospheric forms or fixed by cyanobacteria, the nitrogen concentration varies with biological activity (Li et al., 2004; Scheffer et al., 1993). However, when nutrients enter the lake system faster than they are removed, high levels of nutrients accumulate within the sediments and the water column of the lake, resulting in eutrophication, which is defined by threshold levels of nutrient enrichment within the water column (see Table 1). Eutrophication can occur naturally but is more commonly associated with human activity.

Table 1: The relationship between lake productivity and the average epilimnion total phosphorus concentrations. Adapted from Bennett and Schipanski (2013)

Lake Productivity	Total phosphorus (μg L^{-1})
Oligotrophic	<5
Mesotrophic	5-30
Eutrophic	30-100
Hypereutrophic	>100

Eutrophication can lead to algae blooms which deplete oxygen in the water, leading to an anoxic state, radically altering or damaging the wildlife. A common type of algae found in eutrophic environments is cyanobacteria, which can make the water toxic to humans and other animals (van Oosterhout & Lürling, 2012). These blooms are prevalent during spring or summer and have the potential to damage the ecosystem, making the lake a threat to health and unsuitable for recreation (Akhurst et al., 2004). Eutrophication not only causes environmental problems, but it can also cause economic costs and transnational issues (in lakes shared by multiple countries). It is important to manage the anthropogenic phosphorus and nitrogen inputs into a lake to avoid eutrophication. This

will maintain water quality and keep the ecosystem in a state that satisfies the most values (Smith & Schindler, 2009).

2.2 The Role of Phosphorus

The effect of nitrogen and phosphorus inputs into water systems are not the same, and the total bacterial biomass has a stronger correlation to the concentration of total phosphorus in fresh and marine ecosystems than nitrogen (Li et al., 2004). Production of organic matter within an aquatic environment is a highly selective process, and phosphorus, nitrogen and carbon ratios in plankton tend to average 1:16:106, which is almost mirrored in surrounding waters at 1:15:105. This ratio is maintained because, in an environment containing a deficiency of nitrate relative to phosphate, nitrogen-fixing bacteria will have a competitive edge and increase nitrogen fixation, which will bring the ratio of nitrogen and phosphorus closer to the concentrations within their cells. However, with a relatively high concentration of nitrogen, non-nitrogen fixing organisms will have a competitive edge because nitrogen fixation is an energy sink. Consequently, the amount of fixed nitrogen entering the system will decline, bringing the ratio back to near cellular concentrations (Redfield, 1958; Tyrrell, 1999).

A distinction between limitations caused by these two nutrients is therefore created. Nitrogen entering the system will result in a transient increase of biological production, a proximate response. Addition of phosphorus, on the other hand, increases the available phosphorus and increases nitrogen fixation, resulting in an ultimate or long-term increase in production (Figure 1). Nitrogen will have no long-term effects on the productivity of a system whereas phosphorus will have a sustained and a proportional increase in the productivity of the system (Redfield, 1958; Tyrrell, 1999). This makes phosphorus management essential to mitigate the water quality issues and are key to managing lake eutrophication.

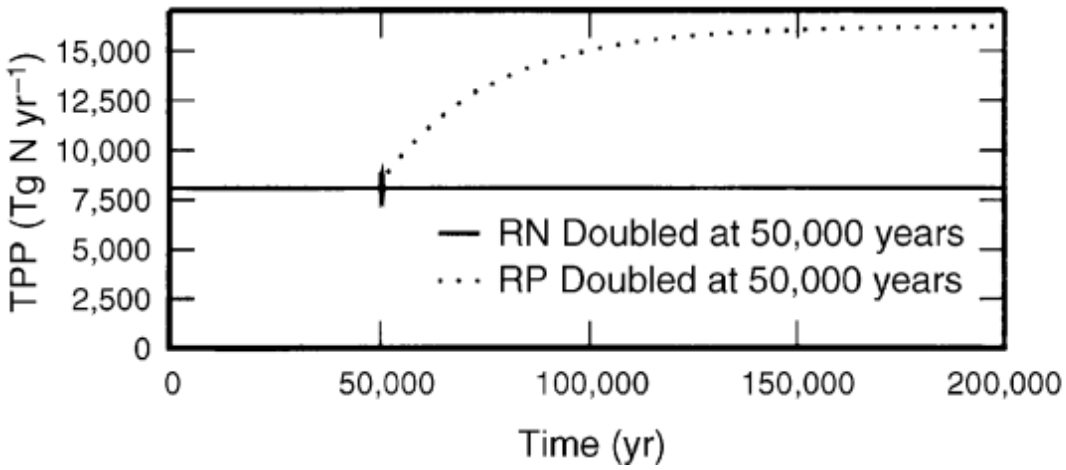

Figure 1 A conceptual model of the effects of doubling river nitrate (RN) and river phosphate (RP) on total primary production (TPP). The graph is showing an increase in

production due to phosphorus increase but no increase in production due to a nitrate increase (Tyrrell, 1999).

2.3 Phosphorus movement into waterways

Phosphorus enters waterways from either point sources or non-point sources. Point sources include stormwater dumping from cities, industrial wastes, sewage dumping, fish farming, or any improper management or animal wastes. New Zealand has strict laws managing the release of phosphorus from point sources, and they do not make up a large portion of the phosphorus entering waterways ("Hazardous Substances and New Organisms Act," 1996). Non-point sources of phosphorus are diffuse and usually made up of the phosphorus lost naturally from the landscape in erosion or runoff within a catchment. Non-Point sources of phosphorus are strongly affected by land use, and the conversion of 14.7 million hectares of native forests over the years since the arrival of humans, and more recently the introduction of superphosphate, has greatly increased the level of phosphorus entering the surface waters of catchments (Dawson, 2007; Kitto, 2010).This loss of phosphorus does not usually factor much in the farming system because it is a relatively small amount of loss, usually below 5% of what was applied (Sharpley et al., 1995). However, this has a large effect on the productivity of the water bodies and is the major cause of the eutrophication of lakes Ellesmere and Forsyth.

2.3.1 Mechanisms driving the movement of phosphorus from non-point sources

Runoff

Runoff is the process of water running over the landscape, and this is usually because of poor infiltration, high relief, or excess water inputs into the landscape (Carpenter, Caraco, Corell, Howarth, Sharpley & Smith., 1998). The water traveling over the landscape can pick up nutrients including phosphorus, and carry them to waterways. The phosphorus in the waterways is either carried as dissolved forms or particulate forms (Bennett & Schipanski, 2013). These processes are especially important in humid environments where overland flow (runoff) contributes the largest phosphorus losses, compared to groundwater flow (Domagalski et al., 2008). Particulate phosphorus is the largest source of phosphorus loss because phosphorus species are not as soluble and easily transported by water compared to nitrates (Canterbury Groundwater Study 2005).

Runoff is affected by many factors and processes, which makes a large-scale assessment of phosphorus losses difficult. This makes it important to identify high-risk transport pathways and to develop models that are complex enough to have predictive capabilities while remaining simple to use (Leone et al., 2008). Some of the factors that affect phosphorus runoff are rainfall amount and

intensity, soil type, soil management, soil phosphorus levels, soil hydrology, and the type of fertilizer and the rate and timing at which it is applied to agricultural land (McDowell et al., 2001; Sharpley & Kleinman, 2003; Shigaki et al., 2007). There are several forms of phosphorus that can be transported by runoff into surface water bodies: Dissolved phosphorus, which includes phosphorus from the soil, and soluble fertilizer losses; Particulate phosphorus is composed of eroded material carrying phosphorus and non-soluble fertilizers such as manure and phosphate rock powder (Sharpley et al., 2002).

Dissolved phosphorus runoff

Dissolved phosphorus from the soil can be determined by the equation:

Dissolved P = extraction coefficient * available soil P * overland flow volume (Sharpley et al., 2002).

Where the available soil phosphorus is affected by past fertiliser applications and natural soil fertility, and the overland flow is affected by climate and infiltration. The extraction coefficient can be affected by land cover. An example of this is pasture providing a more protective layer than crops, resulting in lower soil/ runoff interactions. Other management strategies such as mulching with wheat (*Triticum aestivum*) straw can reduce the extent of water soil interaction by 73% (Sharpley, 1985). In areas where infiltration limits surface runoff, management techniques such as minimum tillage can also improve infiltration rates by increasing soil organic matter content and porosity, which increases soil infiltration and commensurately decreases overland flow (Gilley & Risse, 2000).

Fertilizer applications can also affect dissolved phosphorus losses. The losses from fertiliser depend on the form, method and the timing of the application (Sharpley et al., 2002). Shigaki et al. (2007) found that more soluble forms of phosphorus fertiliser (triple superphosphate, 79% water soluble) significantly increased dissolved phosphorus losses from the soil compared to less soluble forms (Low-grade single superphosphate, 50% water soluble). The lowest losses were recorded from rock phosphate (0.5% soluble). Rainfall event magnitude also had a significant effect on the dissolved phosphorus lost from the system. This indicates that the timing and application rate of phosphorus fertilizer can greatly influence the percentage of dissolved phosphorus lost, especially since a few large storms can account for a large percentage of phosphorus lost in any given year (Cosser, 1989). The method of application can reduce fertilizer losses. Techniques such as knifing or immediate incorporation into the soil by cultivation will prevent the fertilizer from interacting with the surface water flow (Römkens et al., 1973). The depth of runoff interaction increased with increase in soil slope, the kinetic energy of the raindrops, and, to a lesser extent, rainfall intensity (Sharpley et al., 1981).

Particulate phosphorus runoff

The other form of phosphorus lost from soils due to surface runoff is particulate phosphorus. Particulate phosphorus is transported in conjunction with organic or inorganic particles and is usually considered to encompass the vast majority of phosphorus runoff as a result of agriculture **(Bennett & Schipanski, 2013).**

Soil erosion mainly drives particulate phosphorus loss, although it is also somewhat related to dissolved phosphorus losses as the same factors (rainfall intensity, runoff energy and volume, and soil structure) are involved (Sharpley, 1985). These factors increase the entrainment of sediment from fields or natural water channels in the landscape and carry the particulate phosphorus into surface water bodies. It is interesting to note that entrained sediment will usually have a higher phosphorus content than the source material, owing to the preferential transport of finer particles and organic material, which is more adsorbent and contains more phosphorus (Sharpley et al., 2002). This concentrating effect can increase the phosphorus content in runoff sediment by a factor of three (Sharpley, 1985).

Soil erosion is not just created by the entrainment of particles from surface runoff. In the case of unstable landscapes, such as areas where trees are removed landslips can occur which causes large areas to become unstable, exposing soil to the runoff, where it can be carried to water bodies (Reid, Wybrow & Woodward, 2004). Soils can also be exposed to runoff by ploughing, which removes the protective plant layer and loosens the soil exposing nutrient-rich topsoil to erosion and transport. Ploughing can redistribute up to 25 t of soil per hectare per year on a 9◦ slope caused by the increased susceptibility to erosion (Lindstrom et al., 1992).

In the event that cultivation is unavoidable the surface application of organic materials will protect weakly structured soils from raindrop impacts and over the long term increase the levels of soil carbon which will result in a more stable and structured soil, increasing its infiltration and drainage ability, reducing the potential for surface water flow (Rousseva, 1989). Cultivation with the contours of the slope also reduce the velocity of surface flow and reduce its energy, reducing the sediment lost to erosion (McLaren, 1996). The planting of riparian strips can also be used to slow the flow of the surface water (due to resistance) and allow the particulate phosphorus to settle out where it can be absorbed by the riparian plants, preventing loss into waterways (McLaren, 1996).

One pathway for nutrients to enter waterways that is not specifically related to surface runoff but involves particulate phosphorus is when livestock or other animals defecate in the waterway directly. This can be a significant source of phosphorus especially if the animals' range is not limited to the waterway and it concentrates nutrients from a large area. Cattle are problematic in this respect as

they are more likely to defecate when they are walking through a stream (Davies-Colley et al., 2004). Fencing off waterways on farms greatly prevent this from happening.

Subsurface Flows

Unlike runoff which is the surface movement of phosphorus, sub-surface phosphorus transport is the movement of phosphorus through soils. Sub-surface flow can either be matrix flows, or preferential flows, which happen in naturally forming macropores or artificially drained soils. For phosphorus to be transported by sub-surface flows, it must first be moved downwards (leaching) below the soil surface (McDowell et al., 2001). Due to the reactivity of many dissolved phosphorus species, under common phosphorus levels in soils, transport is limited by the short half-life of phosphorus in soil solution (McLaren, 1996). This results in the phosphorus concentrations of water moving through the soil matrix accounting for less phosphorus loss than surface runoff especially when the degree of soil-water contact increases (smaller pores), This is because of increased interaction between the phosphorus and the soil particles (McDowell et al., 2001). However, in certain soil types, management and especially subsurface water flow in artificial drains may be a significant contributor to phosphorus entering surface waterways (Sims et al., 1998).

Sub-surface flow of phosphorus does not occur to a significant degree in all soils, and even soils with pathways that favour sub-surface flow (e.g., tile-drained soils) the surface flows of phosphorus caused greater losses than phosphorus lost by sub-surface flow (Haygarth et al., 1998). The types of soils that are most prone to subsurface drainage and leaching are deep sandy soils that have high phosphorus concentrations from long-term application of excess fertilizer or organic wastes, and soils with high organic matter content (Sims et al., 1998). The reason that these soils are susceptible to subsurface losses is due to the naturally forming preferential flow pathways or the loss of organic phosphorus associated with dissolved organic carbon including fluvic or humic acids (Beauchemin et al., 1998). In soils that have been artificially drained, there is an especially high risk of sub-surface phosphorus losses, as the leachate lost from the system contains dissolved or particulate phosphates (Domagalski et al., 2008). These pathways are particularly important in humid areas where storm events cause massive precipitation which mobilizes a large percentage of phosphorus which is then lost through subsurface flows (Simard et al., 2000). It should be noted, however, that the installation of artificial drains, while it will increase the phosphorus losses in subsurface flow, will decrease the net loss of phosphorus from the system. The drainage will increase water infiltration and reduce overland flow and erosion, which account for most of the phosphorus losses from soils (Simard et al., 2000)

2.3.2 Transport to lakes

Once in a waterway, phosphorus will travel until it is deposited within the river sediment, which generally happens all along the river (McDowell & Sharpley, 2003), however, eventually, the phosphorus ends up at the bottom of the catchment (Figure 2). In most cases, this is the ocean, and the phosphorus will resettle and be buried. In the case of Ellesmere and Forsyth however, the lowest point in a catchment is the lake, and the incoming phosphorus is at concentrations that the system cannot deal with and the water column levels have become high enough to make the lakes eutrophic (Kitto, 2010).

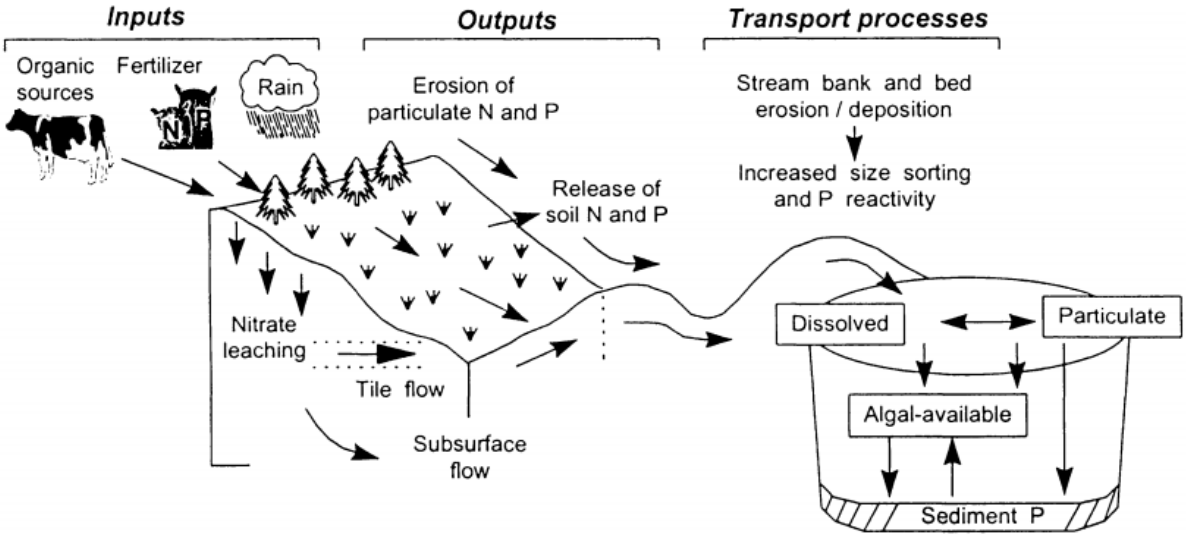

Figure 2 Inputs, outputs and the processes of transport of phosphorus and nitrogen from agricultural land into waterways adapted from (Carpenter et al., 1998)

2.3.3 Transformation of phosphorus at the water-sediment interface

Phosphorus in the form of phosphate is rapidly sorbed onto clay particles within the sediment which results in low amounts of soluble phosphorus in the water (Wang & John Morrison, 2013). A large portion of the insoluble phosphorus will be bound to iron oxides or organic matter. Monbet et al. (2007) studying an Australian lake measured 53% of the total phosphorus was bound to iron (P-Fe) (mainly iron oxyhydroxides) and between 35-55% bound to organic matter, which tended to become mineralised into orthophosphate and subsequently form P-Fe complexes. This indicates that in most systems a large portion of phosphorus will become bound to iron and aluminium, and the chemistry of these phosphorus species will greatly affect phosphorus cycling within an aquatic body.

The P-Fe formed when phosphorus enters a water body is relatively stable and is an equilibrium that strongly favours sorption, in some cases only 3% of total phosphorus is soluble(Webster et al., 2001).

This equilibrium becomes a buffer, maintaining phosphorus levels within the lake and as phosphorus is removed in biological uptake, adsorbed phosphorus is released, forming the 'Phosphate buffer mechanism.' However, the flux of phosphorus out of the sediment can increase when anoxic conditions are created. The amorphous iron oxide layer on clay is strongly dependent on the redox levels in the environment, and strongly anoxic sediments can cause large releases of phosphate and iron into the water column as the oxygen is removed from the iron (Monbet et al., 2007; Webster et al., 2001). Anoxia is an issue in Ellesmere and Forsyth, as brief periods of anoxia do occur in summer, usually only lasting a few hours (Kitto, 2010).

The level of iron oxides, organic matter and other adsorbent species affects the equilibrium of the concentration of phosphorus in the sediment compared to the concentration in solution. The ability of sediment or any amendment to adsorb phosphorus can be defined by an isotherm, that is, the amount of adsorbate (phosphorus) on the adsorbent as a function of its concentration in solution. The gradient of the function is given the denotation K_D and can be used to predict the equilibrium a system will settle into. Measuring the K_D of a substance is a good way to compare different amendments ability to reduce dissolved phosphorus.

2.4 Ellesmere and Forsyth History

Lake Ellesmere (Te Waihora) is a large, shallow brackish water body and Lake Forsyth (Te Roto o Wairewa) is a smaller and less brackish lake (Table 2). They are both separated from the sea by a narrow mixed sand and gravel barrier (Kaitorete barrier) caused by longshore drift (Hemmingsen, 1997). Ellesmere is located on the east coast of New Zealand's' South Island about 40 km south of the city of Christchurch. Forsyth is east of Ellesmere, located in Banks Peninsula.

Table 2 A comparison of Forsyth and Ellesmere. Compiled from: (Hemmingsen, 1997; O'Sullivan, 2017).

Lake	Lake Size	Catchment Size	Salinity	Average depth	Average Temperature
Ellesmere	16,600-23,900 ha	2072 km²	5-8 ppt	1.4 m	16ºC - 23.5ºC
Forsyth	630 ha	109 km²	4 ppt (range: 1-14 ppt)	1.7 m	13.6 ºC (range: 2.4-25.1 ºC)

The values that can be attributed to these two lakes range from cultural and ecological to recreational. The ecological values are primarily due to the position of the lakes, being on the Canterbury plains and near the ocean. The lakes are shallow, and as a result have a very high level of biological productivity, enabling the lakes to support very diverse ecosystems. Additionally, the salinity gradients, occurring as a result of their opening to the sea, the lakes support a wide variety of habitats, which also contributes to biodiversity (Palmer, 1982).

According to oral traditions, the first people to discover the lakes were the Waitaha people led by Te Rakihouia who proclaimed that the lake be called Te Kete Ika a Räkaihautü (the fish basket of Räkaihautü). This resource was prized by successive tribes, and eventually, the lands came under the reign of Ngai Tahu (*Te Waihora Joint Management Plan*, 2004). These natural resources were sources of traditional foods (*Mahinga Kai,* including tuna (eels), patiki (flounder), aua (yellow-eyed mullet) and whitebait), a source of authority, Mana, and as a source of trade. These lakes represent huge social value and part of the history of Ngai Tahu.

The two lakes also provide recreation in the form of fishing, sailing, shooting, and trekking. Forsyth has popular walking and biking tracks, and Ellesmere has fishing (including introduced brown trout), game shooting (the lake supports up to 30,000 waterfowl) and watersports (this has declined due to the lakes shallow nature and the availability of other water bodies) (Palmer, 1982; *Te Waihora Joint Management Plan*, 2004).

2.4.1 Historical state compared to the current state.

Ellesmere

Historically Ellesmere would have been a eutrophic freshwater lake that was significantly larger and deeper, reaching 4-5 metres above sea level. This indicates that the lake had lower nutrient concentrations and lower salinity as the salt and nutrient inputs into the lake would have been more dilute in a larger water body. These factors including the deeper lake would have encouraged a large distribution of freshwater wetlands vegetation and few halophytes (Hemmingsen, 1997). These inferences were confirmed by core sampling carried out by Kitto (2010).

Waihora is currently regarded as being in a hypereutrophic state; it is dominated by algae instead of macrophytes, is a lot more saline and has a lower water level compared to pre-human arrival (Hughey & Taylor, 2008). These changes were brought about by anthropogenic activity and have decreased the values that Ellesmere holds.

The hypereutrophic state has occurred because of the proliferation of agriculture on the Canterbury plains, especially on the rich Waihora wetlands, where drains were set up to reclaim

the land. The most significant increase in nutrients in Ellesmere has occurred from 1970 onwards; this was indicated by analysis of diatoms in lake sediment cores (Kitto, 2010). This increase in nutrient concentration was correlated to the increase in dairy (390%) and beef (73%) in the Canterbury plains (Ballantine & Davies-Colley, 2014). Recent measurements place the dissolved concentrations of phosphorus at 0.2 mg L^{-1} well above the definition of hypereutrophic (Hughey & Taylor, 2008).

The salinity increase and lower water level were driven by the expansion of farmland, as the high lake levels covered a huge area. The lake level is managed by opening the lake to the sea and has been regularly opened since 1947. However, this has reduced the lake area and caused the lake to become much more saline. Although the extent of macrophyte abundance was known to fluctuate prior to 1968, there is no evidence that complete switches from a macrophyte-dominated lake state to a phytoplankton-dominated lake state occurred. However, the low lake level resulted in damage to macrophytes by wind, salt stresses, and the entrainment of sediment. In 1968 the Wahine storm ripped out the macrophytes and suspended sediment, preventing the light from reaching the benthic layer, preventing macrophyte re-establishment (Kitto, 2010).

Forsyth

Lake Forsyth is a recently formed lake. Before European settlement, the lake was a tidal inlet, and in prehistory has cycled between a freshwater, brackish and seawater inlet (Ecan, 2016). Apart from this, there is not much information about the historical nutrient levels in Lake Forsyth. However its catchment comprises mainly of basaltic rocks and melanic soils, which are relatively rich in phosphorus, so it can be assumed that Forsyth would be a highly productive system (O'Sullivan, 2017). Phosphorus loads in the lake have increased, primarily due to the felling of the extensive forests within the Forsythe catchment (Figure 3). The loss of tree cover caused slope stability to decrease, and the slopes became especially vulnerable to tunnel gullying and soil slip erosion, wind, sheet, gully and rill erosion and these forms of erosion would carry phosphorus that would end up in the lake (Taylor, 1996).

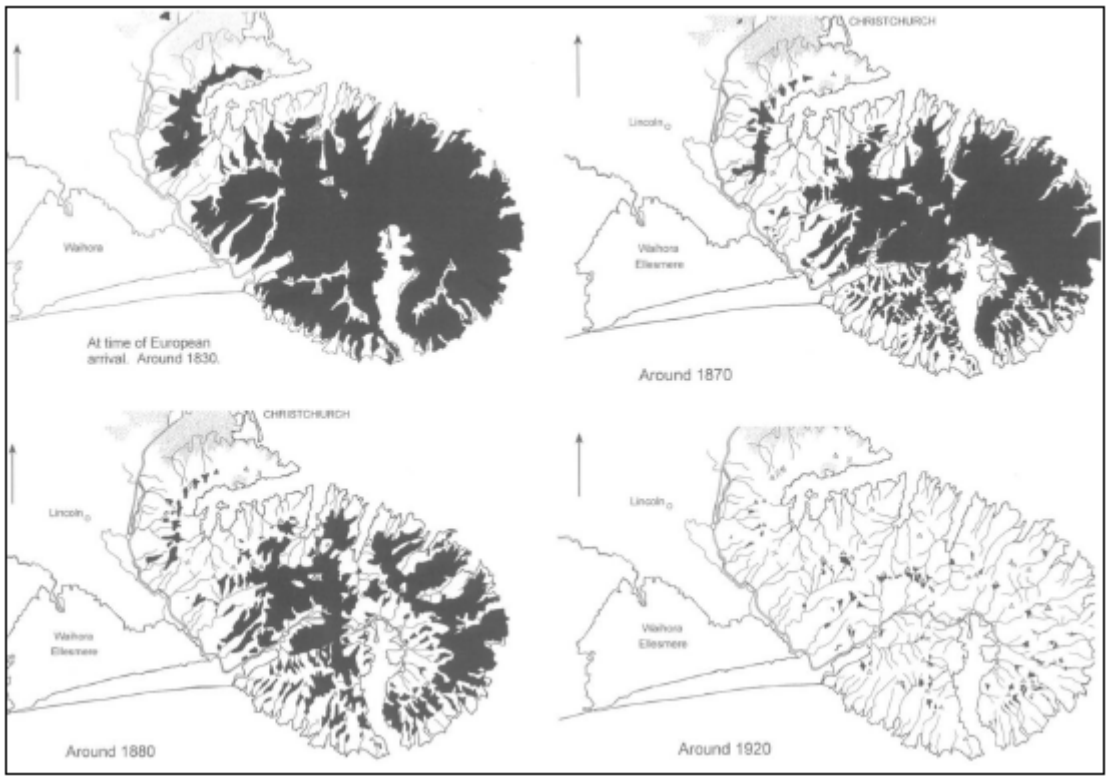

Figure 3 Forest cover on Banks Peninsula from 1830 to 1920 (*Te Waihora Joint Management Plan*, 2004).

Because of the increase in phosphorus the lake has experienced frequent, anthropogenic eutrophication-induced algal blooms since the beginning of the twentieth century (Schallenberg & Schallenberg, 2013). These blooms have begun limiting recreational activities and water usage due to the presence of toxin-producing cyanobacteria (Davie, 2005). The blooms are mainly caused by the hypereutrophic state of the lake with phosphorus concentrations an average of 0.15 mg L^{-1} (Hughey & Taylor, 2008).

Similar to Ellesmere, Forsyth is periodically opened to the sea to flush dissolved nutrients into the ocean. However, this also increased the lake salinity and causes stress to lake biota, limiting the diversity of species present (Schallenberg et al., 2003)

2.4.2 Management options

It would be difficult to return the lakes to its previous level and salinity, as this would require, less frequent lake opening, which would flood private land in Canterbury. It would also alter the ecosystems again, back to freshwater, which would reduce the environments suitable for halophytic plants, such as saline herb fields and mudflats, which may decrease the lake's ecological value (Kitto, 2010). However, the reduction of nutrient (particularly phosphorus) levels within the lake are achievable. The management of phosphorus levels within a lake come under two main approaches. The first is pre-emptive, reducing the amount of phosphorus entering

the lake. The second is remedial, finding a way to immobilise the phosphorus within the sediment so that it is no longer available for algal growth.

Pre-emptive

Pre-emptive strategies mainly revolve around reducing phosphorus entering the lake by targeting pathways, and due to variable landscapes and climates, there is no one method to solve the issue. Reductions can be seen when farmers incorporate best management practices. The most common of which are below:

Fencing off waterways on farms, preventing effluent overloading and planting riparian strips will reduce the amount of overland runoff of animal waste and organic phosphorus to waterways. Also, these methods will take up excess dissolved phosphorus and slow the flow rate of surface runoff, allowing particulate phosphate to settle. In addition, maintaining good soil structure, maintaining soil cover, ploughing with the contours are proposed methods to improve infiltration and control runoff energy. This reduces the amount of particulate phosphorus and organic phosphorus being carried by erosion into waterways. (Jenkins, 2016; Reid et al., 2004; Schallenberg et al., 2010; Smith & Schindler, 2009). This will increase the sub-surface flow of dissolved phosphorus, especially in areas with tile drainage, however the net loss will be reduced (Haygarth et al., 1998).

Remedial

Recently there has been interest in removing phosphorus from the water column by using amendments such as allophane, Phoslock™, and Bauxsol™. These amendments are generally clay structures that have a strong affinity to phosphorus and remove phosphorus from the water column through anion exchange or adsorption. (Akhurst et al., 2004; Spears et al., 2016) This paper will focus on remediation of New Zealand coastal lakes with these potential amendments.

2.5 Potential Remedial Amendments

2.5.1 Likely effects of adding immobilising agents

While reducing the nutrient load flowing into Forsyth and Ellesmere is a worthy endeavour, the amount of phosphorus leaving the system is low, as the majority of phosphorus entering a lake will end up bound to aluminium, or iron. Monbet et al. (2007) states that during anoxic conditions the phosphorus will be released from the iron oxides into the water. This causes the phosphorus to cycle from lower layers in the sediment into higher layers, thus reducing phosphorus burial, and keeping phosphorus in the water-sediment interface. These processes result in the so-called 'phosphorus buffer,' which can cause a time lag between a reduction of phosphorus entering the waterbody and a reduction in water nutrient levels. In the New South Wales lakes it was predicted that with normal

sediment loads it would take an estimated 8-22 years for the phosphorus to be buried and water quality to improve (Monbet et al., 2007). Because burial in sediments usually represents the only significant long term sink for phosphorus in the aquatic environment, finding a way to keep phosphorus adsorbed to the sediment through varying conditions is necessary for improving water quality (Monbet et al., 2007; Welch & Cooke, 1995).

One method of inactivating P, is the use of an amendment, which can either bind and flocculate the phosphorus allowing it to be scavenged from the water column. Amendments can also be used as a capping agent that prevents phosphorus from being released from the sediment by adsorbing it (Gibbs et al., 2010). This would likely prevent the release of phosphorus during anoxic periods, limiting algal growth and preventing blooms. Amendments in conjunction with catchment management could thereby reduce the lake to a mesotrophic level. There are several phosphorus flocculants/capping agents, several of which are described below:

2.5.2 Allophane

Allophane precipitates in soils where silicon and aluminium are present in solution at sufficient concentrations, forming the transient poorly crystalised material that has a high specific surface area (predicted at 800 m2 g^{-1} (Parfitt, 1990)) and typically a surface charge (Harsh et al., 2002) which increases the surface area available to react with phosphorus. Throughout the 1980s, allophanes' definition changed a few times, and allophane is now seen as 'clays sized minerals with a short-range order containing silica-alumina and water in chemical combination.' This excludes the related imogolite due to its tubular structure compared with allophone's short spherical morphology. (Allen & Hajek, 1989; Harsh et al., 2002; Parfitt, 1990)

Due to its unique shape and composition, allophane has a high specific surface area, and unusual charge characteristics (having both permanent and variable charges). This affects its influence on soil properties such as structure, cation/anion exchange capacity and contaminant mobility by reacting strongly with not only metal cations but also water, dissolved anions various organic molecules, and soil minerals (Harsh et al., 2002). The predominant interest of the current study with regard to allophane is its high retention of orthophosphate (Figure 4). Phosphate retention is achieved in two main reactions: a faster formation of aluminol (Al-OH) complexes within and around the spheroidal structure of allophane and the slower precipitation of aluminium phosphates being released by the meta-stable allophane (Harsh et al., 2002).

The adsorption of phosphates onto the surface aluminol groups is important for this study as the formation of inner-sphere phosphate surface complexes leads to phosphate being occluded from lake sediment pore water, making it non-bioavailable (Harsh et al., 2002). This makes allophane a

candidate for adsorbing phosphates within coastal lakes in order to reduce phosphorus levels. adsorption to external aluminol groups can also contribute to the total phosphorus binding capacity but will be less effective, as the phosphate can be re-released into the water column (Parfitt & Henmi, 1982).

The ability for allophane to adsorb phosphorus may be limited by the pH of its environment. The most reactive groups on the clay's surface are $Al(OH)H_2O$, which are susceptible to modifications by pH, becoming $Al(OH_2)$ $+H_2O$ and $Al(OH)OH^-$ in acid and alkaline environments respectively. This results in acid environments creating more sites to bind anions; between pH 5-7 both positive and negative sites are present(Parfitt, 1990). This may lead to allophane being ineffective in P adsorption at high pH, reducing its effectiveness for coastal lakes, many of which have high pH due to influxes of sea water. Gibbs et al. (2010) found that this was the case, with allophane adsorbing 9.5 g of phosphorus per kilo of allophane at pH 8.9 but adsorbing 16g kg^{-1} at pH 7.

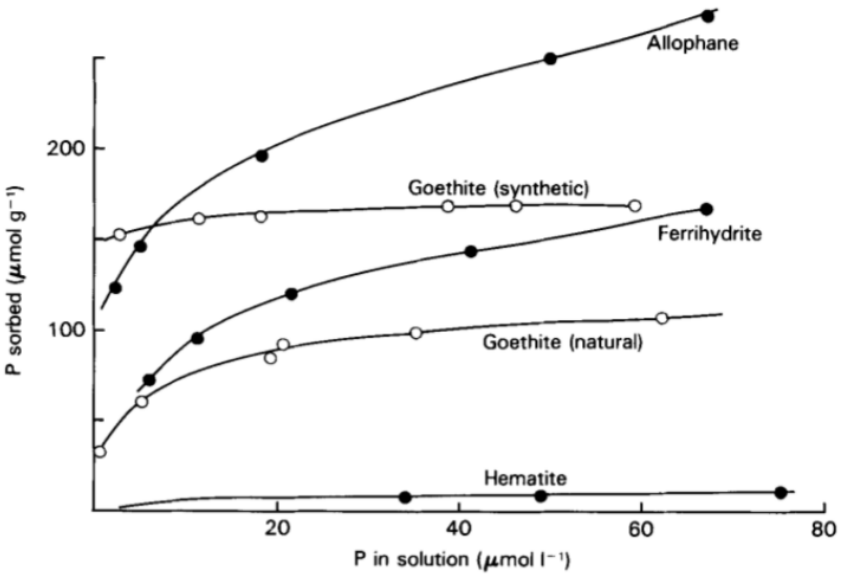

Figure 4 Comparing the sorption curve of allophane against iron-based minerals. (1g of mineral at 250C, 16 hours shaking (R. L. Parfitt, 1989).

2.5.3 Phoslock™:

Phoslock™ is a product developed by the **Commonwealth Scientific and Industrial Research Organisation** (CSIRO) and the Australian Water and Rivers commission as part of an effort to redress the increase of phosphorus that contributed to the eutrophication of the Swan River estuary in Western Australia (Douglas et al., 1999). Phoslock™ is a lanthanum modified bentonite clay. It is produced by reacting lanthanum chloride with bentonite clay, in which the lanthanum substitutes

most of the sodium on exchange sites on the clay, along with some magnesium and calcium (NICNAS, 2001). Lanthanum reacts with phosphate in solution to form lanthanum phosphate, an insoluble form of phosphorus which effectively removes the phosphate from the water column.

2.5.4 Bauxsol™

Bauxsol™ is a trademark of Virotec International Ltd for a geochemically and physically modified red mud, produced from the processing of bauxite to create aluminium. It has been repurposed for environmental management including binding phosphates (Lin et al., 2002). Because of the variables in the processing stage, Bauxsol™ can have slightly different mineralogy. However, it is a deep red mud that usually comprises 25-35% hematite, 5-20% hydrated alumina, 15-35% sodalite, and 4-10% calcium minerals according to Virotec's Material Safety Data Sheet (MSDS). Its mineralogy confers an abundance of magnesium, calcium, and aluminium exchange sites on a large surface area, which can bind, complex and adsorbs a large variety of oxyanions. Also, it is composed of minerals that are not viewed as environmentally hazardous, increasing its viability as a remediation candidate. McConchie et al. (2000) found that due to iron reduction, Bauxsol™ was ineffective at binding phosphorus in anoxic lakes.

2.5.5 Other amendments

Alum

The most common lake water treatment is alum. This forms a floc within alkaline waters and removes impurities by forming a capping layer over the sediment. This works effectively, however, in lakes with high incoming sediment or macrophyte senescing, the floc will be buried and no longer be effective (Welch & Cooke, 1999). In New Zealand coastal lakes such as Ellesmere/ Te Waihora, there tends to be a lot of resuspension of sediment due to wind action (Hughey & Taylor, 2008). This will also resuspend the floc and prevent proper remediation. However in acidic conditions, alum will cause aluminium phosphates to precipitate out of solution, and in neutral conditions, aluminium hydroxide groups form which can adsorb phosphorus (Cooke & Kennedy, 1981). However Lake Ellesmere and Forsyth are alkaline and within this environment dissolved aluminate would form, which would not be effective at removing phosphorus from the waterbody. Accordingly, it was not considered in this study.

Aqual-P

Aqual-P is a zeolite clay based amendment developed by Blue Pacific Minerals (BMP). Aqual-P looks promising as it outperformed all the other amendments (Phoslock™, Alum, allophane) by a factor of two in acid conditions (Gibbs et al. (2010), and performed better than allophane in alkaline

conditions, possibly due to the charge being less variable than that of allophane. This product combines the natural phosphate absorbing properties of zeolites with Al-doping, to promote P precipitation and Al hydroxide adsorption reactions making it chemically similar to alum and allophane. The aluminium is not released, which reduces potential toxicity, and acidification problems. Interestingly the zeolite clay also absorbs other nutrients such as nitrate and ammonium (Yang et al., 2004). However, there are very few studies considering the use of Aqual-P, additionally, the aluminium hydroxides will likely mimic the activity of allophane. For these reasons, it was omitted from the experiment.

2.6 Aims of the Experiment

The aim of this study then is to analyse allophane, Bauxsol™, and Phoslock™ in-vitro to identify their potential for phosphate sequestration in coastal lakes and water bodies, compared to other control clays. This will be achieved by creating adsorption isotherms at varying pHs and comparing the adsorption potential of the amendments. This will enable the identification of the most effective amendment for the remediation of Forsyth and Ellesmere.

Chapter 3

Methodology

3.1 Experimental Design

3.1.1 pH and eC survey

A survey of lake water pH and electrical conductivity (eC) was carried out on the 7/08/2017 while the lakes were closed off from the ocean. Access points to the lake were identified that were most accessible (Figure 5). Samples were collected by wading out into the lake to get to a point that was undisturbed by the shore wave action, and a sampling stick with a cup attached to the end, enabled the collection of water far enough away to be unaffected by sediment disturbed by the sampler. The eight samples were collected and each placed into a 50ml centrifuge tubes and labeled. Within 24 hours the samples were taken to the lab and measured for pH (Mettler Toledo GmbH SevenEasy pH) and electrical conductivity (eC) (Mettler Toledo AG FIveEasy™ FE30).

3.1.2 Experiment one, pH sensitivity.

Experiment 1 was designed to provide a rapid assay of pH sensitivity of the P-adsorbing characteristics of the amendments. For Allophane, Bauxsol™, Phoslock™, and Kaolinite (control) amendments, 0.15 g of amendment was weighed to an accuracy of ± 0.0005 g was added to 50 ml centrifuge tubes, each containing 40 ml of a solution of fixed concentration (25 mg L^{-1}) of phosphate-phosphorus made using deionized water. 0.1ml of 1M HCl, 0.1M HCl, DI water, 1M NaOH and 0.1M NaOH, were added to 5 tubes respectively. The tubes were agitated for an hour then left to sit for at least 24 hours. Centrifuging was not required. The pH of the samples was then measured with the Mettler Toledo pH meter. Phosphate levels were measured using the ascorbic acid method (absorbance at 880nm λ) (WFE & APHA, 2005) using the calibration curve determined by several pilot tests using lake water (0.005 0.05 0.25 0.5 1 mg L^{-1}). The curve was created using a Shimadzu UV-vis Spectrophotometer Model: UV-mini 1240. The detection limits were between 1mg L^{-1} and 0.005 mg L^{-1}. Measurements above the level of the calibration curve were achieved by diluting the sample by either a factor of 10 or 100 before the addition of the reagent. Each sample also included a blank. Due to their high buffering capacity, the pH of Bauxsol™ and allophane did not reach lower pHs, and the experiment was repeated for the two amendments, but this time the concentration of acids they received were: 0.1ml of 2.5M HCl, 5M HCl, and 10M HCl.

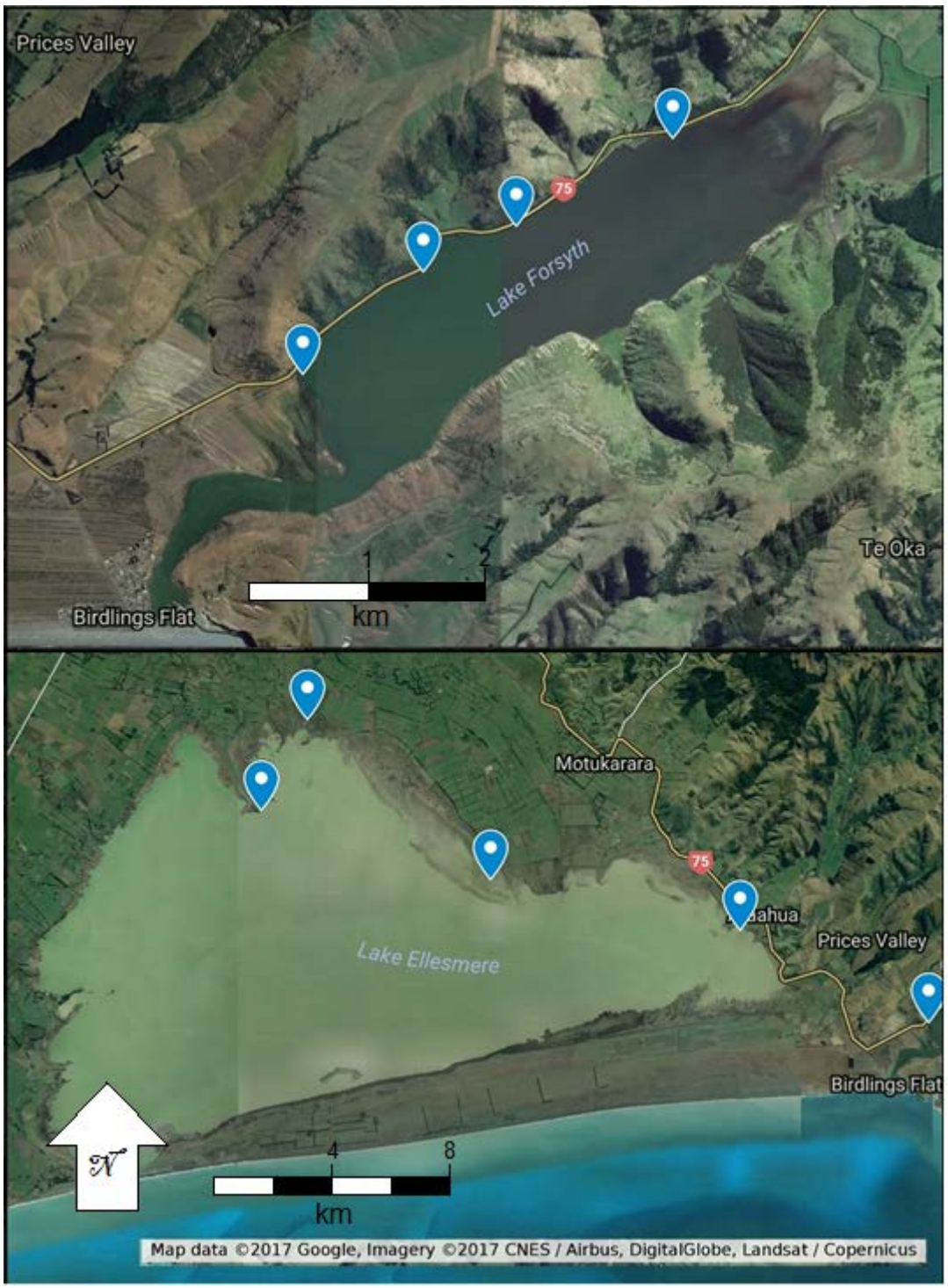

Figure 5: Sites in Lake Ellesmere and Forsyth where sampling was carried out.

3.1.3 Experiment two, Determining K_D.

A common method to compare the ability of different sorbents is to create an isotherm or the amount of adsorbate (in this case phosphorus) as a function of its concentration in the surrounding liquid at a constant temperature. In general, isotherm functions show a rapid rise in the adsorption capacity with an increase in the solution concentration, but then eventually plateau as sorption sites

are saturated, and equilibrium is reached. The sorption curves are commonly fitted with Freundlich or Langmuir functions. However, the initial slope does not significantly change with the increase of the solute concentration and can be approximated by a straight line. The gradient of that line gives a good approximation of the adsorbed concentration as a function of the dissolved concentration (Zamparas et al., 2015). Comparing these values indicate the effectiveness of the amendments. This method was used to compare the potential amendments.

For each amendment sample including several control clays (kaolinite, bentonite, illite), 0.15 of clay measured to an accuracy of ± 0.0005g was added to 50ml centrifuge tubes, containing 40ml of varying solutions of phosphate phosphorus (0.005, 0.05, 0.5, 5, 25 and 50 mg L^{-1} Phosphate- P in deionized water). The tubes were agitated for an hour then left to sit for at least 24 hours for the phosphate to adsorb to the amendments. The samples were then centrifuged at 3000rpm for 5 minutes to settle the clays out of suspension. Once the clays were settled, the phosphate levels were measured using the previously described method. The pH of the final solutions were measured, to identify any changes caused by the amendment. Each sample was replicated twice and also included a blank. However, the lack of variation between replicates indicated that it was not necessary for the next experiment.

For Allophane, Bauxsol™ and Phoslock™ 0.15 g of clay measured to an accuracy of ± 0.0005g was added to 50ml centrifuge tubes, each containing 40ml of phosphate solutions of varying concentration (0. 5, 1, 5, and 12.5 mg L^{-1} Phosphate- P). To each of the tubes 0.1ml of 1M HCl, was added to reduce the pH. The tubes were agitated for an hour then left to sit for at least 24 hours. Centrifuging was not required. The pH of the samples was then measured with the Mettler Toledo pH meter. The solutions were then measured for phosphorus levels using the previously described method. In this experiment, the phosphorus levels were reduced to better estimate lake concentrations of phosphorus because the 50 mg L^{-1} phosphate concentrations were too high above naturally occurring lake phosphorus levels to be relevant.

3.2 Statistics

In Experiment one, the aim was to indicate the pH at which the amendments were most effective, and a statistical test was not needed, just a visual analysis. Data from experiment one was included in the statistical analysis of experiment two, however.

The data for each of the amendments was plotted, and a regression line (including the standard error) was fitted by Microsoft Excel Statistics package. The slope of the predicted line (the sorption coefficient, K_D) was calculated, along with the standard error. The standard error was used to compare the clays and identify which had a significantly greater sorption ability. The standard errors

of the slope of the two regression lines (K_D) of each amendment were compared to identify if there was a significant difference between the two slopes, and identify the effect of a reduced pH on the adsorption capacity.

Chapter 4

Results

4.1 Lake pH and eC survey

The average pH and eC for Ellesmere, including standard errors were **8.3 ± 0.4** and **5.9 ± 1.4** respectively**. T**he average pH and eC for Forsyth were **8.9 ± 0.2** and **2.0 ± 0.1** respectively (Table 3)

Table 3: The pH and eC of Ellesmere and Forsythe in four locations.

Lake	Co-ordinates	pH	eC (mS cm^{-1})
Ellesmere	-43.744, 172.44887	7.5	6.17
Ellesmere	-43.71683, 172.46788	8.33	3.18
Ellesmere	-43.76477, 172.54354	9.22	9.78
Ellesmere	-43.77984, 172.64664	8.01	4.34
Forsythe	-43.78988, 172.76288	8.94	1.714
Forsythe	-43.79648, 172.74668	9.02	2.16
Forsythe	-43.79986, 172.7371	9.08	2.23
Forsythe	-43.80752, 172.72464	8.07	2.04

4.2 Experiment 1: pH sensitivity

Experiment 1 indicated that Bauxsol™'s and allophane's capacity to adsorb phosphorus are very sensitive to pH, The ratio between the initial phosphorus concentration and final concentration reduced by an order of magnitude as the pH dropped from 8 to 4.5. At high and low pH's Bauxsol™ and allophane appear to have released phosphorus as the ratio is greater than one. Phoslock™'s phosphorus binding capacity remained relatively stable around pH that would be found in a lake. The control (kaolinite) was also relatively unaffected by the pH level, and in fact, released more phosphorus into solution across all pH levels (Figure 6).

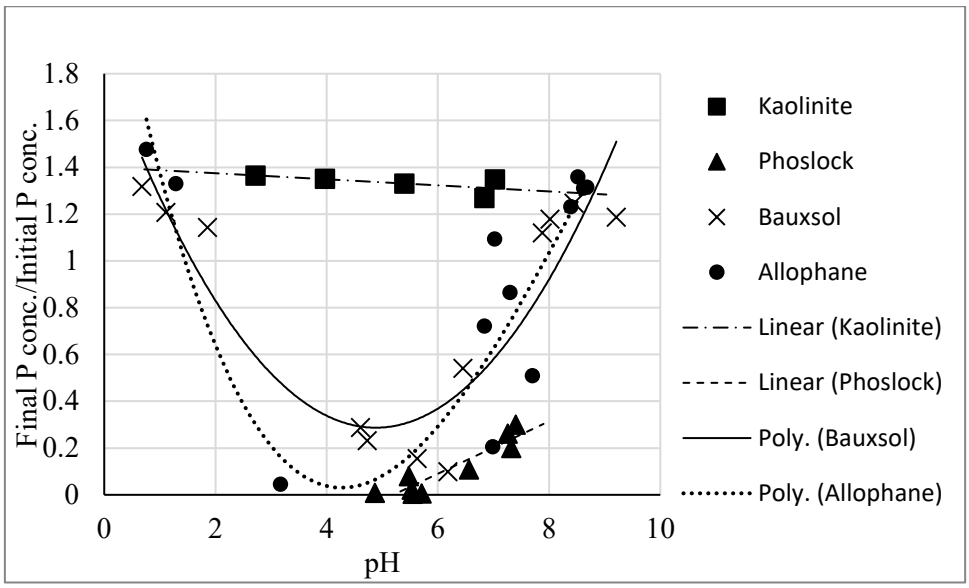

Figure 6 The effect of pH on the adsorbance of phosphate by kaolinite, Phoslock™, Bauxsol™ and allophane showing the variability of the responses of various amendments.

4.3 Experiment 2: The effect of pH on K_D

4.3.1 K_D of the clays at an unmodified pH.

Phoslock™ had the highest K_D, significantly higher than Bauxsol™ and allophane ($P \leq 0.05$). Bauxsol™ is indistinguishable to the controls kaolinite and bentonite (Figure 7). The pH of the neutral DI water used in the experiment was altered by the application of the clays. The pHs measured were kaolinite at 5.4, Bauxsol™ at 8.02, allophane at 8.52 and Phoslock™ at 7.26.

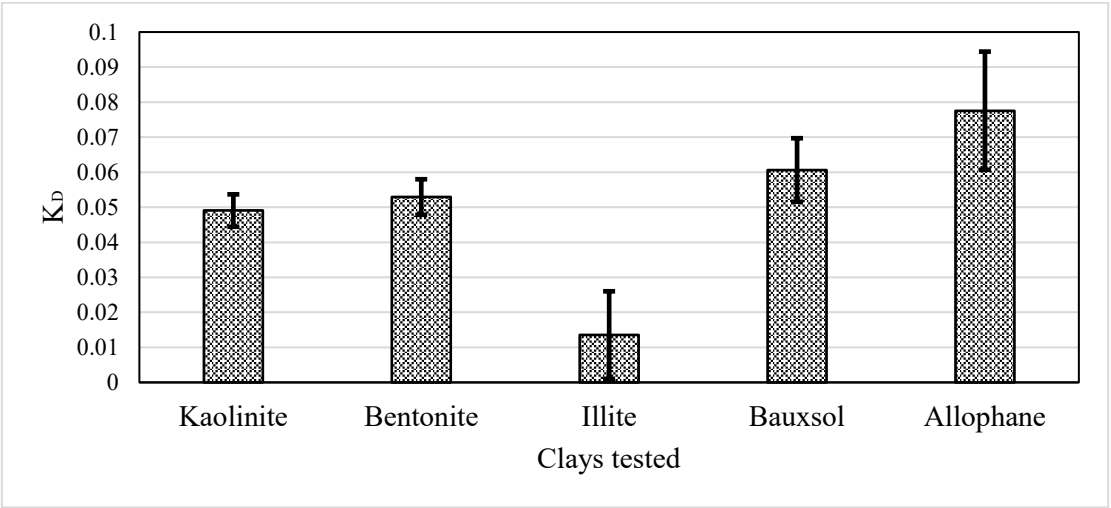

Figure 7 : Comparison of the KD of 6 clay amendments at unaltered pH to identify potential phosphorus adsorbents (including standard error). PhoslockTM is not included as it had a KD of 141.0 with an S.E. of 38.5, much too large to fit on the graph.

4.3.2 Allophane

As seen in Figure 8, when placed into phosphorus solution the allophane adsorbs a large fraction of the dissolved phosphorus. The level at which allophane adsorbed the phosphorus in experiment 1 was estimated and from this K_D (the gradient of the line) was calculated to be 0.08 ± 0.02 S.E. (The Y intercept is -0.34 ± 0.44). The same process was carried out for the results of allophane in experiment 3 and the K_D calculated was 0.26 ± 0.06 S.E. (The Y intercept is -0.25 ± 0.38) (Figure 8). The regression line fit for pH 8.5 had a probability of fit of P=0.14, partially due to data points needing to be omitted due to levels below the detection limit of 0.005mg L^{-1} (, reducing the statistical power of the test. The regression line fit for allophane in pH 7.2 was significant with P<0.05. Despite the lack of significance of the pH 8.2 graph, the difference between the two lines, taking into account the standard error, it is clear that allophane significantly increases its adsorption ability in more acidic environments.

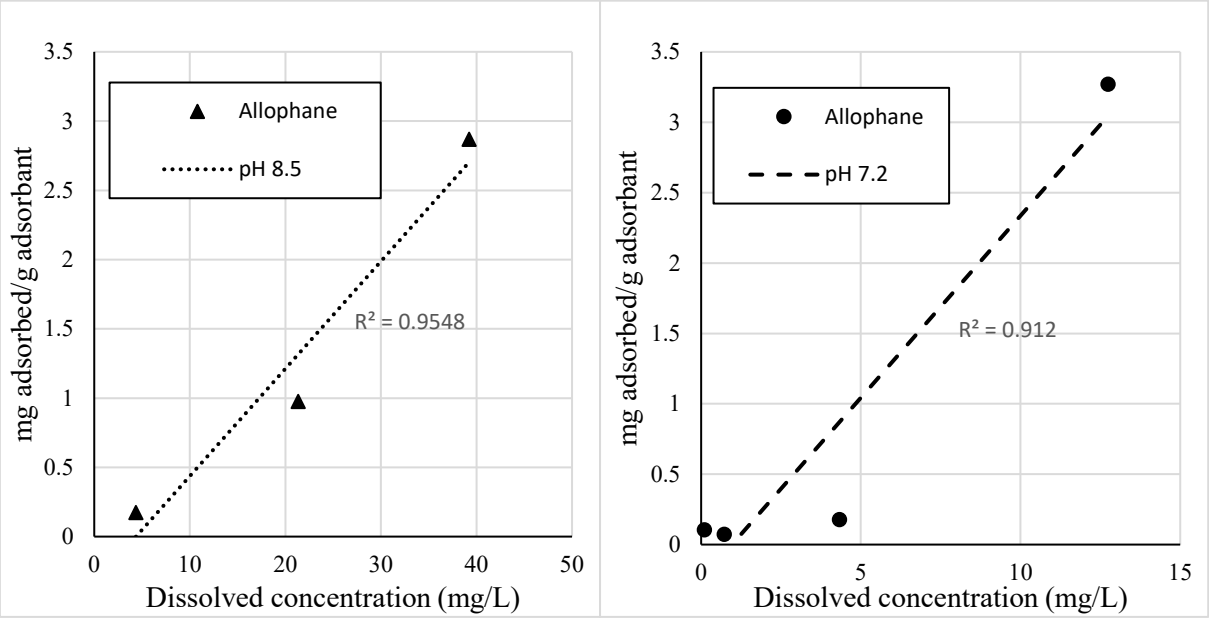

Figure 8. Phosphate -P adsorption isotherms for allophane at pH 8.52 (caused by the addition of allophane) and at pH 7.17 (0.1 ml of 1M HCl added to the centrifuge tube).

4.3.3 Bauxsol™

As seen in Figure 9, when placed into phosphorus solution the Bauxsol™ adsorbs a portion of it. From these data, in experiment 1 the K_D (the gradient of the line estimating the trend) was calculated to be 0.06 ± 0.01 S.E. (Intercept 0.01 ± 0.19). The same process was carried out for the results of Bauxsol™ in more acidic conditions and the K_D calculated was 2.56 ± 0.42 S.E. (Intercept -0.43 ± 0.31) (Figure 9). The regression line fits for both experiment 1 and experiment 3 significantly (P<0.05).

Taking into account standard error, the adsorption rate of Bauxsol™ significantly increased in more acidic environments.

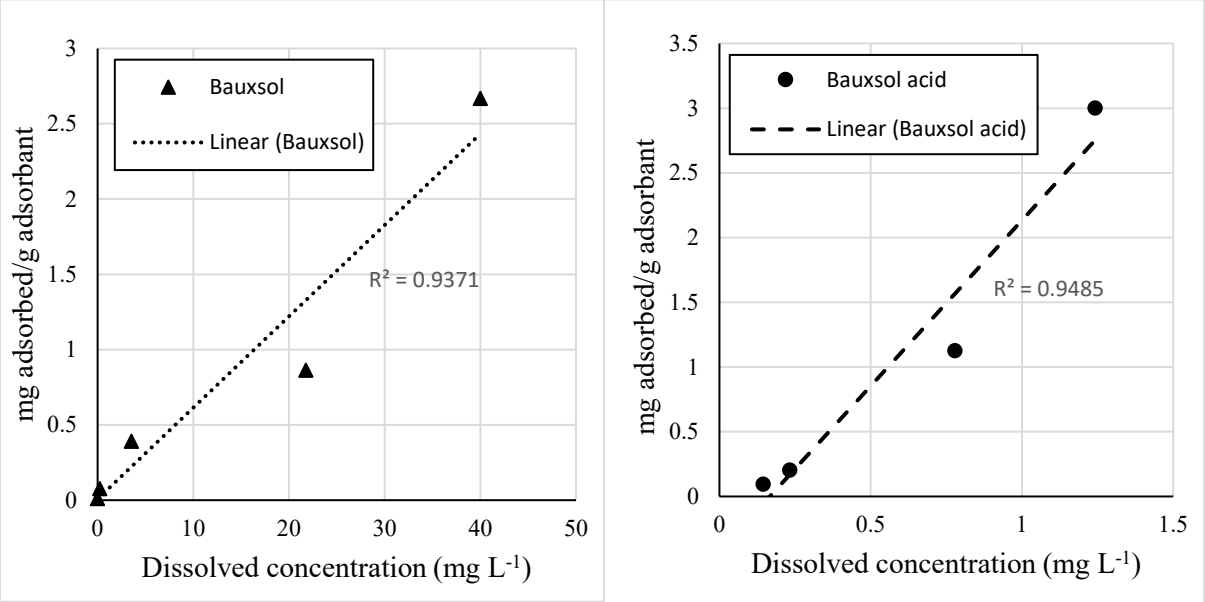

Figure 9 The Phosphate-P adsorption isotherm of Bauxsol™ at pH 8.02 (Caused by the addition of Bauxsol™ to the solution), and at pH 5.52 (0.1 ml of 1M HCl added to the centrifuge tube).

4.3.4 Phoslock™

As seen in Figure 10 when placed into phosphorus solution the Phoslock™ adsorbs a portion of it. From the data at pH 7.3, the K_D can be estimated to be 141.0 ± 38.0 S.E. (Intercept -0.41 ± 0.20). The same process was carried out for the results of Phoslock™ at pH 5.4, and the K_D was calculated to be to be 42.0 ± 6.8 S.E. (Intercept -0.12 ± 0.35). The regression line fit at both pH 7.3 and pH 5.4 was significant ($P<0.05$). Taking into account standard error, the adsorption rate of Phoslock™ significantly decreased in more acidic environments.

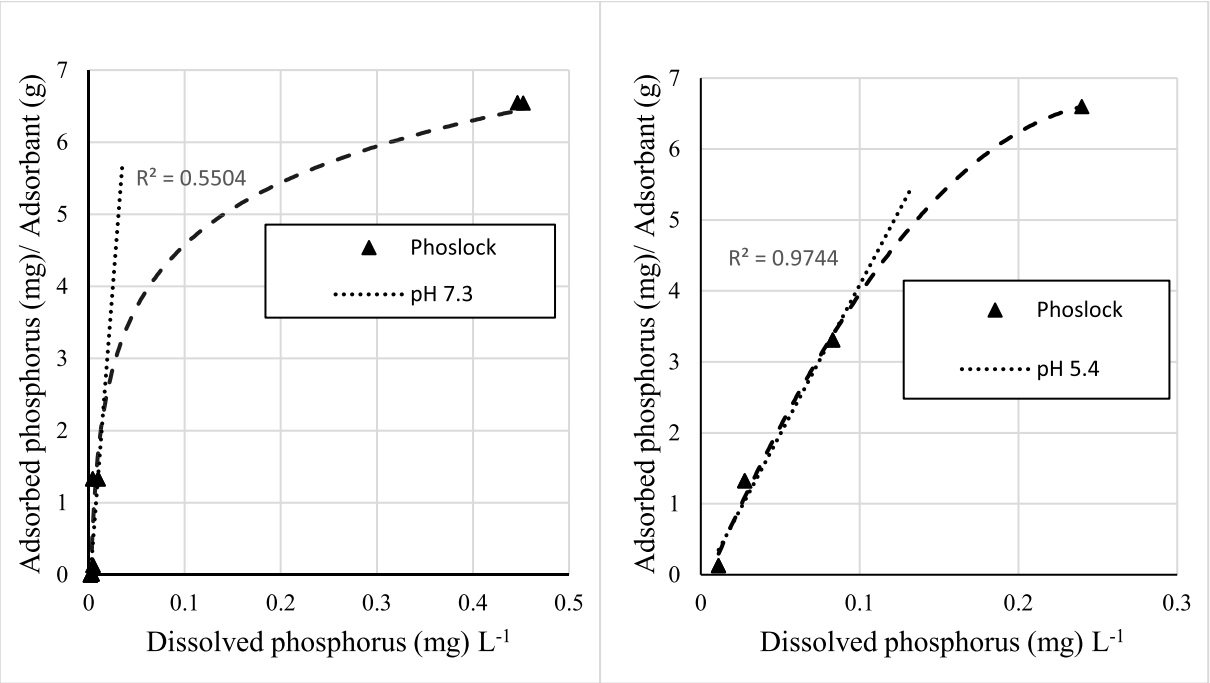

Figure 10. The adsorption isotherm of Phoslock™ at pH 7.3 (minimal change caused by the addition of Phoslock™ to the solution) and at pH 5.4 (0.1 ml of 1M HCl added to the centrifuge tube). The K_D curves are estimated at lake relevant concentrations by the straight-line regression.

4.3.5 The effect of pH on K_D

Figure 11 shows the summary of the results of experiment 2. Phoslock™ has a K_D an order of magnitude higher either Bauxsol™ or Allophane. At the higher pH, Bauxsol™ and Allophane have indistinguishable K_D. However, when acid is added to the solution, the pH of Bauxsol™ dropped by a larger amount, and its adsorption response was significantly greater than that of allophane.

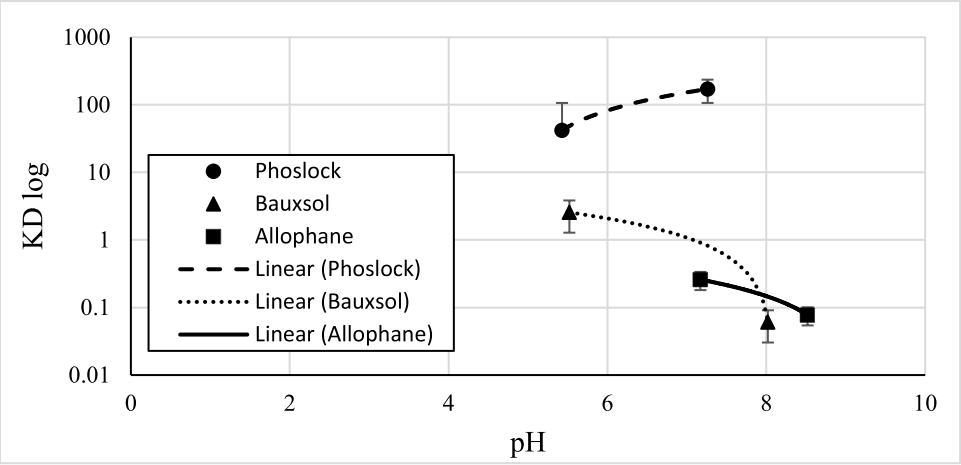

Figure 11. A graph is comparing the effect of the pH of the solution on the K_D of the three most promising amendments. The K_D axis was logged due to the large difference between Phoslock™ and the other two amendments (allophane and Bauxsol™).

Chapter 5

Discussion

5.1 What the Results Show and reasons

5.1.1 Survey

The pH of Ellesmere and Forsyth is between 8 and 9, which is significantly alkaline. This is likely an indication of seawater intrusion. However, this is not the only explanation because Forsyth had a significantly lower eC (an indicator of salinity) than Ellesmere but has a higher pH. This is confirmed in other studies where Forsyth has a lower average (4 ppt) salinity than Ellesmere (5-8 ppt) (Hemmingsen, 1997; O'Sullivan, 2017). The lower salinity indicates that there are other processes increasing the pH of the lake. The fluctuations of the lake pH will be driven by the opening of the lakes to the sea which is alkaline. The opening of the lakes also reduces water levels, and this causes sediment to be more readily entrained by waves, reducing light penetration and suffocating macrophytes (Kitto, 2010). This system then favours algae growth with high photosynthetic rates that can utilize dissolved carbon dioxide, removing it from the water and causing an increase in pH (Kurano et al., 1995). Therefore any amendment that is used in either lake needs to have a stable adsorption ability in alkaline water.

5.1.2 KD and Adsorption and the effect of pH

Controls:

Without adding any acid to the samples, bentonite and kaolinite have similar K_D values to Bauxsol™. However, this was because the addition of Bauxsol™ caused the samples to become alkaline, which reduced its adsorption ability. When pH was taken into account kaolinite was not responsive and remained at extremely low K_D level. This indicates that the amendments have a significantly higher K_D than common clays.

pH dependence:

In the second experiment, the amendments' dependence on pH was identified, and it showed that kaolinite and Phoslock™ were only minimally affected by pH. However, unlike Kaolinite, Phoslock™ adsorbed the majority of the phosphorus in the solution. Allophane and Bauxsol™ were very pH dependent. Below pH 2 or above pH 7.5 Bauxsol™ and allophane were only slightly more effective than the control clays. Allophane and Bauxsol™ are both aluminium rich compounds and will form aluminol groups, these functional groups are what gives the amendments their charge and

adsorption capacity (Harsh et al., 2002), however similar to alum, these groups are very pH dependent, and this causes Bauxsol™ and allophane to have variable charges. This means that their highest adsorption capacity occurs between pH 5.5 and 7 (Parfitt, 1990). Acid-activated Bauxsol™ has also been tested, and it has been found to increase adsorption capability by more than 700% due to the surrounding water becoming acidic.(Ye et al., 2016). The lanthanum phosphate that forms from Phoslock™ is very stable and does not dissolve between pHs 5 to 9 a range that encompasses the pHs of both Ellesmere and Forsyth.

Bauxsol™

Of the three amendments, Bauxsol™ had the lowest K_D in a pH similar to what would be found in Forsyth or Ellesmere. This makes it ineffective for the purposes of the study. However, when the pH was reduced, Bauxsol™ was more effective than allophane (it was still an order of magnitude below Phoslock™). Contrarily Akhurst et al. (2004) found that Bauxsol™ outperformed Phoslock™ in oxic waters. However, this may have been due to the acidic state of the lake. This indicates that Bauxsol™ would be effective in acidic lakes, but not in the lakes under study. The susceptibility of Bauxsol™ to an anoxic release of phosphorus and iron also makes it less effective in Ellesmere and Forsyth due to the short periods of anoxia that occur during summer (Kitto, 2010). Bauxsol™'s large phosphorus binding capacity could also be utilized in acidic or neutral lakes that are shallow and well aerated, without significant periods of anoxia. It would be especially useful for fragile ecosystems, as it only contains minerals that would be found in the environment and does not introduce any foreign substances (Lin et al., 2002).

Allophane:

Allophane had the lowest K_D out of the three amendments when acid was added to the samples. Because of its Aluminol groups, allophane was not effective above pH 7.5. However, it was an effective sorbent for phosphorus under acidic conditions (compared to the controls). Allophane, unlike BauxsolTM, does not release phosphorus under anoxic conditions, due to its spherical morphology where adsorbed phosphates are occluded from the environment making it not redox sensitive (Gibbs et al., 2010; Parfitt, 1990). Allophane may be a possible amendment for neutral or acid lakes, which are subject to periods of anoxia and since it is a naturally forming clay, it will be perceived as a non-disruptive amendment. Allophane can be obtained in a relatively pure form from New Zealand Soils. However, these sources may not be sufficient to obtain the quantities needed to treat a lake, and would contain phosphates making it inappropriate for use as an amendment (Parfitt, 1990). Synthetic allophane may prove a better alternative. However it is very expensive to produce in the laboratory, and a commercial source would have to be sought as economies of scale may be able to reduce the cost of production (Huang et al., 2016; Ohashi et al., 2002).

Phoslock™

Regarding $K_{D,}$ Phoslock™ was orders of magnitude above allophane and Bauxsol™. The lanthanum doping forms clay that rapidly adsorbs the majority of the dissolved phosphorus. Phoslock™ is, therefore, a very powerful binding agent for phosphorus. However, it does pose some difficulties. Following applications of Phoslock™, lanthanum concentrations significantly increased in the top 8cm of the lake sediment (Meis et al., 2012). The adsorption of phosphorus leads to a partial release of lanthanum, with levels of 1.2–4.2 mg m^{-3} detected (Gibbs et al., 2010). It should be noted, however, that at these concentrations there were no adverse effects detected, and though there was a significant increase of lanthanum in the livers and hepatopancreas of rainbow trout and koura(crayfish), there was no significant increase in their flesh, and levels returned to normal within six months of application (Landman & Ling, 2011). Phoslock™ can be utilized in either acid or alkaline lakes, including anoxic environments. This makes Phoslock™ the most attractive option for eutrophic coastal New Zealand lakes.

The main reason Phoslock™ is so effective is the stability of the $LaPO_4$ produced. Phoslock™ is stable at pH 5-11, which will encompass the majority of natural water bodies, and results in low phosphorus re-release (NICNAS, 2001). Reitzel et al. (2012) concluded that even in anoxic conditions the phosphorus would remain bound to Phoslock™. Another study found that 79% of the phosphorus bound by Phoslock™ was unlikely to be released from the sediment even under reducing conditions and within a pH range of 5-9 (Meis et al., 2013). Also, the application of Phoslock™ reduced the cycling phosphorus by increasing the mass of phosphorus permanently bound to sediment (Meis et al., 2013).

5.2 Potential use in Lake Ellesmere and Forsyth.

In the Phoslock™ adsorption isotherm, the graph began curving over as the adsorption sites were saturated, this gives an indication of the total mass of phosphorus that can be adsorbed by the amendment. This means that the rate required to reduce the nutrient levels in the water column can be estimated.

The total amount of phosphorus in a lake can be defined as:

$\mathbf{P_{T1} = [P_S]M_S + [P_{W1}]V_W}$ (before the amendment is added)

$\mathbf{P_{T2} = [P_S]M_S + [P_{W2}]V_W + [P_A]M_A}$ (with amendment added)

Where P_T (1 and 2) is total phosphorus (g); $[P_S]$, $[P_W]$ and $[P_A]$ are the concentrations of phosphorus in the sediment, water column and amendment respectively (mg g^{-1}); and M_S, M_W and M_A are the masses of sediment water column and amendment respectively (g).

The variables $[P_S]$ and $[P_A]$ can also be defined by their relationship to $[P_W]$ using the K_D:

$$\mathbf{[P_S] = [P_W]\, K_{DS}}$$

$$\mathbf{[P_A] = [P_W]\, K_{DA}}$$

Using the conservation of mass (as no phosphorus has been added to the system):

$$\mathbf{P_{T1} = P_{T2}}$$

Or:

$$\mathbf{[P_S]M_S + [P_{W1}]V_W = [P_S]M_S + [P_{W2}]V_W + [P_A]M_A}$$

Substituting in the K_D equations:

$$\mathbf{K_{DS}[P_{W1}]M_S + [P_{W1}]V_W = K_{DS}[P_{W2}]M_S + [P_{W2}]V_W + K_{DA}[P_{W2}]M_A}$$

Factorised into:

$$\mathbf{[P_{W1}]\,(K_{DS}\,M_S + V_W) = [P_{W2}]\,(K_{DS}\,M_S + V_W + K_{DA}M_A)}$$

This can be rearranged into:

$$\frac{[\mathbf{P_{W1}}]}{[\mathbf{P_{W2}}]} = 1 + \frac{\mathbf{K_{DA}M_A}}{\mathbf{K_{DS}\,M_S + V_W}}$$

Where $\frac{[\mathbf{P_{W1}}]}{[\mathbf{P_{W2}}]}$ is equal to the ratio of phosphorus in the water before and after the application of the amendment.

Example for use in Lake Ellesmere:

Reducing Ellesmere from a hypereutrophic state (~0.1 mg L^{-1}) to mesotrophic (~0.01 mg L^{-1}) (see table 1), requires the reduction of the dissolved phosphorus by a factor of 10 (the concentrations are at a ratio of 10:1):

$$\mathbf{10} = \mathbf{1} + \frac{\mathbf{K_{DA}M_A}}{\mathbf{K_{DS}\,M_S + V_W}}$$

With an average depth of 1.4m, each m^2 of Ellesmere contains 1400 Litres of water. Phoslock has a neutral K_D of ~140.

Assuming that the top 0.05m of sediment interacts with the water column, has a similar K_D to kaolinite (0.05) at neutral- alkaline pH, and a bulk density of 500,000g m^{-3}. The amount of Phoslock™ required to create mesotrophic conditions in each square metre of Ellesmere can be calculated with:

$$\mathbf{M_A} = \frac{\mathbf{9\ (K_{DS}\ M_S + V_W\ )}}{\mathbf{K_{DA}}}$$

Where K_{DS} = 0.05, M_S = (500,000 g m^{-3}*0.05 m^3 = 25,000 g), V_W = 1400 and K_{DA} = 140

It would take 170.4 g of Phoslock™ to reduce the phosphorus levels to mesotrophic in 1 m^2, or 1.7 t of Phoslock™ per ha^{-1}.

With a cost of $1700 USD per tonne (including freight from the factory in China), and Ellesmere's surface area of 200 km^2 34,000 t would be needed which would cost $57.8 M USD.

Examples of successful Phoslock™ use:

Lürling and van Oosterhout (2012) reported on Groene Eiland, a 5-ha enclosed pond (claustrum) within a 220 ha water body that was created in the Netherlands and provided a perfect experiment and control to test Phoslock™. After treatment of Phoslock™ cyanobacteria levels were significantly lower

in the claustrum than the surrounding control area which experienced a massive algal bloom. Macrophyte beds also developed in the claustrum, and filterable lanthanum from the Phoslock™ dropped below the Dutch safety standard within five days of the application.

Meis et al. (2012) tested Phoslock™ in a 9-ha reservoir with an application of 2.5 t ha^{-1} which increased the total phosphorus sorption capacity of the lake by 250kg, further testing indicated that 79% of the phosphorus adsorbed to the Phoslock™ was unlikely to be released in natural conditions. That result was similar to another study which found that the addition of Phoslock™ significantly decreased dissolved phosphorus and the iron-bound phosphorus in the sediment. It also increased the HCl extractable phosphorus, a measure of the phosphorus bound to the lanthanum (Reitzel et al., 2012)

5.3 Future Studies and Improvements, What is the Next Logical Step

It is recommended that future studies are carried out that look at whether sodium chloride, present in many coastal lakes including Forsyth and Ellesmere, affects the effectiveness of Phoslock™. The K_D of the sediments in the lakes and the depth of their interaction need to be studied to confirm the rates of application needed to create a mesotrophic state within the lake. This cost also could be reduced if it was found that Ellesmere was naturally eutrophic, resulting in the less Phoslock™ being needed.

The desorption, adsorption rates also need to be studied. Phoslock™ will not work if it only adsorbs dissolved phosphorus, as the P-Fe will continue to be released from other clays in anoxic conditions, the next step in the study would be to identify what happens when Phoslock™ is mixed with sediments and the transfer of phosphorus between them.

Chapter 6

Conclusion

Allophane and Bauxsol™ are promising amendments for neutral or acidic lakes: they adsorb significant amounts of P and contain naturally occurring minerals. However, Ellesmere and Forsyth are alkaline, which renders those amendments ineffective. In contrast, Phoslock™, a synthetic amendment, is effective in either acid or alkaline lakes, making it the most efficacious option for eutrophic coastal New Zealand lakes. Phoslock™ also has the highest K_D of the three amendments by a factor of 10. A 1-tonne application per hectare would reduce the available phosphorus in the Ellesmere and Forsyth water column to below hypereutrophic levels (0.03 mg L^{-1}). There have been numerous successful treatments of water bodies including in Australia and the Netherlands, giving this technology credibility. It would take 170.4 g of Phoslock™ to reduce the phosphorus levels to mesotrophic in 1 m^2, or 1.7 t of Phoslock™ per ha^{-1}.

With a cost of $1700 USD per tonne (including freight from the factory in China), and Ellesmere's surface area of 200 km^2 34,000 t would be needed which would cost $57.8 M USD. The K_D of the sediments in the lakes and the depth of their interaction need to be studied to confirm the rates of application needed to create a mesotrophic state within the lake. This cost could be reduced if it was found that Ellesmere was naturally eutrophic, resulting in the less Phoslock™ being needed.

In tandem with efforts to reduce phosphorus entering the lakes, there is also the possibility of effectively removing the phosphorus that is currently in the lake with Phoslock™, and improve the cultural, recreational, and ecological values of Te Waihora and Te Roto o Wairewa.

Appendix A

Collected Data

Number	Amendment (0.15g)	PO4 concentration (mg/L)	additive (0.1ml)	additive concentration (M)	pH final	Modifier	Sample concentration (mg/L)
1	Kaolinite	0.005	#N/A	#N/A	#N/A	1	-0.011
2	Kaolinite	0.05	#N/A	#N/A	#N/A	1	0.039
3	Kaolinite	0.5	#N/A	#N/A	#N/A	1	0.562
4	Kaolinite	5	#N/A	#N/A	#N/A	10	0.437
5	Kaolinite	25	#N/A	#N/A	#N/A	100	0.202
6	Kaolinite	50	#N/A	#N/A	#N/A	100	0.423
7	Kaolinite	0.005	#N/A	#N/A	#N/A	1	0.006
8	Kaolinite	0.05	#N/A	#N/A	#N/A	1	0.061
9	Kaolinite	0.5	#N/A	#N/A	#N/A	1	0.540
10	Kaolinite	5	#N/A	#N/A	#N/A	10	0.417
11	Kaolinite	25	#N/A	#N/A	#N/A	100	0.199
12	Kaolinite	50	#N/A	#N/A	#N/A	100	0.425
13	Bentonite	0.005	#N/A	#N/A	#N/A	1	0.242
14	Bentonite	0.05	#N/A	#N/A	#N/A	1	0.405
15	Bentonite	0.5	#N/A	#N/A	#N/A	1	0.715
16	Bentonite	5	#N/A	#N/A	#N/A	10	0.446
17	Bentonite	25	#N/A	#N/A	#N/A	100	0.204
18	Bentonite	50	#N/A	#N/A	#N/A	100	0.415
19	Bentonite	0.005	#N/A	#N/A	#N/A	1	0.337
20	Bentonite	0.05	#N/A	#N/A	#N/A	1	0.413
21	Bentonite	0.5	#N/A	#N/A	#N/A	1	0.702
22	Bentonite	5	#N/A	#N/A	#N/A	20	0.237
23	Bentonite	25	#N/A	#N/A	#N/A	100	0.197
24	Bentonite	50	#N/A	#N/A	#N/A	100	0.419
25	Illite	0.005	#N/A	#N/A	#N/A	1	-0.149
26	Illite	0.05	#N/A	#N/A	#N/A	1	0.042
27	Illite	0.5	#N/A	#N/A	#N/A	1	0.570
28	Illite	5	#N/A	#N/A	#N/A	10	0.514
29	Illite	25	#N/A	#N/A	#N/A	100	0.196
30	Illite	50	#N/A	#N/A	#N/A	100	0.472
31	Illite	0.005	#N/A	#N/A	#N/A	1	-0.017
32	Illite	0.05	#N/A	#N/A	#N/A	1	0.038
33	Illite	0.5	#N/A	#N/A	#N/A	1	0.571
34	Illite	5	#N/A	#N/A	#N/A	10	0.518
35	Illite	25	#N/A	#N/A	#N/A	100	0.207
36	Illite	50	#N/A	#N/A	#N/A	100	0.474
37	PhoslockTM	0.005	#N/A	#N/A	#N/A	1	0.002
38	PhoslockTM	0.05	#N/A	#N/A	#N/A	1	0.003
39	PhoslockTM	0.5	#N/A	#N/A	#N/A	1	0.004

40	PhoslockTM	5	#N/A	#N/A	#N/A	1	0.009
41	PhoslockTM	25	#N/A	#N/A	#N/A	1	0.454
42	PhoslockTM	50	#N/A	#N/A	#N/A	100	0.166
43	PhoslockTM	0.005	#N/A	#N/A	#N/A	1	0.003
44	PhoslockTM	0.05	#N/A	#N/A	#N/A	1	0.003
45	PhoslockTM	0.5	#N/A	#N/A	#N/A	1	0.007
46	PhoslockTM	5	#N/A	#N/A	#N/A	1	0.005
47	PhoslockTM	25	#N/A	#N/A	#N/A	1	0.451
48	PhoslockTM	50	#N/A	#N/A	#N/A	100	0.160
49	BauxsolTM	0.005	#N/A	#N/A	#N/A	1	-0.011
50	BauxsolTM	0.05	#N/A	#N/A	#N/A	1	-0.018
51	BauxsolTM	0.5	#N/A	#N/A	#N/A	1	0.181
52	BauxsolTM	5	#N/A	#N/A	#N/A	10	0.328
53	BauxsolTM	25	#N/A	#N/A	#N/A	100	0.197
54	BauxsolTM	50	#N/A	#N/A	#N/A	100	0.375
61	Allophane	0.005	#N/A	#N/A	#N/A	1	-0.026
62	Allophane	0.05	#N/A	#N/A	#N/A	1	0.020
63	Allophane	0.5	#N/A	#N/A	#N/A	1	0.496
64	Allophane	5	#N/A	#N/A	#N/A	10	0.421
65	Allophane	25	#N/A	#N/A	#N/A	100	0.191
66	Allophane	50	#N/A	#N/A	#N/A	100	0.370
67	Kaolinite	25	NaOH	1	7.03	100	0.284
68	Kaolinite	25	NaOH	0.1	6.84	100	0.266
69	Kaolinite	25	H2O	0	5.4	100	0.283
70	Kaolinite	25	HCl	0.1	3.97	100	0.287
71	Kaolinite	25	HCl	1	2.72	100	0.289
72	PhoslockTM	25	NaOH	1	7.4	100	0.021
73	PhoslockTM	25	NaOH	0.1	7.32	100	-0.004
74	PhoslockTM	25	H2O	0	7.26	100	0.014
75	PhoslockTM	25	HCl	0.1	6.56	100	-0.026
76	PhoslockTM	25	HCl	1	4.87	100	-0.051
77	Allophane	25	NaOH	1	8.68	100	0.277
78	Allophane	25	NaOH	0.1	8.62	100	0.273
79	Allophane	25	H2O	0	8.52	100	0.285
80	Allophane	25	HCl	0.1	8.39	100	0.253
81	Allophane	25	HCl	1	7.7	100	0.076
82	BauxsolTM	25	NaOH	1	9.21	100	0.245
83	BauxsolTM	25	NaOH	0.1	8.45	100	0.259
84	BauxsolTM	25	H2O	0	8.02	100	0.242
85	BauxsolTM	25	HCl	0.1	7.88	100	0.230
86	BauxsolTM	25	HCl	1	6.45	100	0.083
87	BauxsolTM	25	HCl	2.5	1.86	100	0.275
88	BauxsolTM	25	HCl	5	1.11	100	0.288
89	BauxsolTM	25	HCl	10	0.68	100	0.313
90	Allophane	25	HCl	2.5	3.17	1	1.136
91	Allophane	25	HCl	5	1.29	100	0.316
92	Allophane	25	HCl	10	0.76	100	0.351
93	PhoslockTM	0.5	HCl	1	5.53	1	-0.006

94	PhoslockTM	1	HCl	1	5.48	1	0.067
95	PhoslockTM	5	HCl	1	5.55	1	0.013
96	PhoslockTM	12.5	HCl	1	5.71	1	0.068
97	BauxsolTM	0.5	HCl	1	4.61	1	0.164
98	BauxsolTM	1	HCl	1	4.73	1	0.258
99	BauxsolTM	5	HCl	1	5.63	1	0.797
100	BauxsolTM	12.5	HCl	1	6.18	1	1.225
101	Allophane	0.5	HCl	1	6.84	10	0.055
102	Allophane	1	HCl	1	7.02	100	0.118
103	Allophane	5	HCl	1	7.3	100	0.026
104	Allophane	12.5	HCl	1	6.99	1	0.089

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